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## DISCLAIMER

# MATERIALS FOR OPTICAL COATINGS IN THE UV*

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## ABSTRACT

We used 248-nm, 20-ns laser pulses to measure laser-damage thresholds for halfwave-thick single layers of 15 potential UV coating materials, for highly reflective coatings made of 13 combinations of these materials and for antireflective coatings made using 5 combinations of the materials. Refractive index, absorption, position of the UV absorption edge, stress and environmental stability were measured for the halfwave-thick single layers. The first three of these parameters are closely related and were generally correlated with damage thresholds of the single-layer coatings. Thresholds of HR coatings were

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correlated with absorption in the high-index materials used in the coatings and with refractive index of the low-index materials. Thresholds of AR films were not well correlated with properties of single-layer coatings.

## I. Introduction

In response to a growing need for damage-resistant optical coatings for UV lasers, we conducted a survey study designed to answer two questions: (1) Are laser-damage thresholds of single-layer films correlated with other measurable properties of the films? (2) Are thresholds of multilayer high reflector (HR) and antireflection (AR) coatings correlated with either the thresholds of single layers of the materials from which the coatings were fabricated or the physical properties of the individual materials? Positive answers to these questions would provide a needed systematic procedure for the selection of UV coating materials. Our previous studies of UV coatings made of $SiO_2$, $MgF_2$ and $Sc_2O_3$ indicated that considerable time and expense were required to optimize deposition of a single coating material.[1,2] A random selection of materials for development might either prevent or slow the study of the best candidates.

In light of the above, it was not certain that a survey study would produce the most useful results. Surveys, by definition, involve testing only a few films of each material. At the outset, the optimum deposition parameters may not be known for each material. In addition, thresholds of single-layer films might be dominated by the characteristics of the substrate surface. Therefore, the results of a survey might not represent the potential of all of the various materials studied.

To increase the probability of obtaining useful results, we attempted to determine the physical characteristics associated with high thresholds in coatings, rather than simply to identify the best materials.

Both physical parameters and laser-damage thresholds were measured for single layers of 15 materials, and thresholds were measured for both AR and HR coatings made from these materials. The results of this study are presented here and indicate that the survey was moderately successful in identifying correlations between large thresholds and relevant physical parameters.

## II. Coating Deposition

All coatings used in this study were deposited by Optical Coating Laboratory, Inc. (OCLI) using electron-beam evaporation. Single-layer films and AR coatings were deposited onto fused silica substrates whose surfaces were fabricated at OCLI by bowl-feed polishing. The HR coatings were deposited onto conventionally polished substrates of BK-7 glass. A cursory study of deposition parameters was made for materials that had not previously been well-studied, but in the spirit of the survey, we did not attempt extensive optimization.

Single-layer films of most materials had good cosmetic appearance. Exceptions were films of $YF_3$ which were sometimes crazed by stress failure, films of $Na_3AlF_6$ which contained some streak-shaped flaws that were probably due to improper substrate cleaning or to environmental degradation, and some films of $ZrO_2$ and NaF which had a generally hazy appearance when backlighted with intense white light. Similar characteristics were also observed in HR coatings made with those materials, and some cosmetic flaws were also present in reflectors made of $ThO_2/MgF_2$ or with $HfO_2$ as the high-index material.

## III. Measurement of Physical Properties of the Coatings

Properties other than laser-damage thresholds were measured at OCLI. Transmittance and reflectance were measured with a Cary 17-DX spectrophotometer. Index of refraction for films of the individual materials was calculated from the measured reflectance and transmittance spectra of thick single layers. Stress was determined by interferometric measurements of stress-induced flexure of coated substrates 0.38 mm thick. The extinction coefficient of each material was measured by coating a half-wave film of the material over an HR coating and observing the decrease in reflectance. Therefore, scattering loss as well as absorption was included in this measurement.

The absorption band edge was defined to be the wavelength at which transmittance was 50% for a coating with an optical thickness of 372 nm (1.5 wavelengths at $\lambda$ = 248 nm). Some materials had band edges below 200 nm, the wavelength limit of the spectrometer. These materials were separated into two groups: those with no detectable absorption at 200 nm (band edge much less than 200 nm) and those with measurable absorption at 200 nm (band edge less than 200 nm).

The films were subjected to standard environmental evaluation consisting of abrasion and adhesion tests, and 24 hours of exposure to high humidity.

The physical properties measured for the halfwave-thick films are given in Table 1. The measured extinction coefficient k (imaginary part of n+ik) was generally small in the fluorides, except for $Na_3AlF_6$ and NaF, for which the high level of scattering masked the absorption, and generally large in the oxides, except in $Al_2O_3$ and $SiO_2$, two oxides which have absorption edges below 200 nm. Stress was very large in several materials, including $YF_3$, in which stress may have been partially relieved by crazing. Two oxide materials, MgO and $Al_2O_3$, failed the environmental test. While it has traditionally been difficult to control the deposition of MgO, environmental failure of $Al_2O_3$ is unusual and was not anticipated.

## IV. Measurements of Laser-Damage Thresholds

Damage thresholds were measured at Lawrence Livermore National Laboratory with 20-ns, 248-nm pulses generated by a discharge-pumped KrF laser. This damage facility has been described in detail elsewhere.[1] At the surface of the sample, the beam was 1.5 mm in diameter at the $e^{-2}$ intensity level, but the fluence distribution was nonuniform. The highest fluences in the beam occurred at isolated maxima, where the fluence was uniform to within 5% over areas not less than 0.1 mm in diameter. For each shot, the fluence distribution was photographed with Kodak 1-Z spectroscopic plates, and the fluence distribution was determined by densitometry. Absolute fluence for each shot was computed by numerically integrating the fluence distribution and normalizing the distribution so that the integral agreed with measured pulse energy.

An average of seven test sites on each sample were irradiated once each. Nomarski interference microscopy was used to photograph each site (at a magnification of 420X), both before and after the site was irradiated. Sites were also inspected visually using the unaided eye and intense white-light backlighting, and with both Nomarski and bright-field microscopy. Damage was defined to be a permanent surface alteration detectable by any of these inspection techniques.

Threshold was defined to be the average of the highest fluence that did not cause damage and the lowest fluence that caused damage. Thresholds were sharply defined in most films, particularly those with low thresholds. In a few coatings with high thresholds, the spacing of worst-case defects was comparable to the size of the hot spots in the beam. For such samples, there was a range of fluences as large as 30% of threshold over which damaging and nondamaging fluences were mixed, and threshold determinations for such films were less certain.

## V. Damage Thresholds for Single-Layer Coatings

Thresholds for two halfwave-thick films of each material are given in Fig. 1. The thresholds ranged from less than 1 J/cm$^2$ in $ZrO_2$, which is comparable to the threshold of some metallic films, to 25 J/cm$^2$ in $ThF_4$ which is about twice the fluence required to induce damage on bare polished surfaces of fused silica.[3] The latter is an unusual result; thresholds of coatings seldom exceed those of bare polished surfaces. However, the observation we are reporting is straightforward. Using the damage procedure described above, we find (1) thresholds ranging from 9 to 15 J/cm$^2$ for bare silica surfaces; (2) thresholds exceeding 20 J/cm$^2$ for silica surfaces coated with some low-index films; and (3) the same damage morphology for surfaces of both types--small pits surrounded by halos, thought to be caused by contact of laser-induced plasma with the optical surface.

In Fig. 2 we compare the measured thresholds with physical properties of the films. Thresholds were correlated with extinction coefficient and with position of the absorption edge, which are closely related parameters. There was also a general correlation between refractive indices and thresholds, but thresholds were independent of stress. The influence of environmental stability on thresholds is uncertain. Films of $Na_3AlF_6$ and NaF failed environmental testing and had thresholds below those of other low-index materials; films of $Al_2O_3$ and MgO also failed environmental tests, but had threshold comparable with those of other oxides.

Our experimental results are generally similar to those of Newnam and Gill who used 22-ns, 266-nm pulses to test single layers of six oxide and three fluoride materials[4], and to those of Walker et.al. who tested single layers of six oxides and three fluorides using 15-nm, 266 nm pulses[5]. In all three studies, thresholds were largest for films of low-index materials that were highly transparent at wavelengths below 200 nm. However, there is a considerable range in thresholds reported in these three studies for films made of a particular material, and no consistent threshold ranking of the several materials. We conclude that survey studies give a general indication of the relationship of various material properties to thresholds, but may be ineffective in establishing the merits of a given material.

Finally, our results should be compared to proposed scaling relationships for damage thresholds. A correlation between refractive index and damage threshold was first reported by Turner[6] and later developed into a scaling law by Bettis et.al.[7]. Their scaling law relates the applied optical electric field strength at threshold $E_t$ to atomic number density N, index of refraction n, the electronic charge $q_e$, the permeativity $\epsilon_o$, and a critical electron displacement $X_{cr}$:

$$E_t = \frac{N}{n^2-1} \frac{q_e}{\epsilon_o} X_{cr}. \qquad (1)$$

The derivation of this rule is based on the assumption that the applied optical field interacts directly with the electrons, so the scaling rule would be most applicable to damage by direct ionization or by avalanche ionization. More recently, Lange et.al.[8] have proposed a model based on the assumption that damage results from heating of inclusions. Their calculations suggest that the threshold fluence $J_t$ is related to the bulk properties of the material in which the inclusion is buried:

$$J_t \propto T_m\sqrt{C_pKt}, \tag{2}$$

where $T_m$, $C_p$, K and t are respectively, the melting temperature, specific heat, thermal conductivity and the duration of the laser pulse.

Neither of these rules adequately describes our data. The square roots of the thresholds in Fig. 1 are randomly distributed when plotted against the factor $N/(n^2-1)$ with values of n taken from Table 1. This is not unexpected because correlations in Fig. 2 suggest that damage at 248 nm is more closely related to absorption than to avalanche. There is an apparent correlation between the thresholds in Fig. 1 and the term $T_m\sqrt{C_pKt}$ from Eq. 2. Thresholds for most fluoride coatings fall on one curve when plotted against $T_m\sqrt{C_pKt}$; thresholds for oxides fall on one of two curves. A model based on heating of inclusions is further suggested by the fact that threshold damage in many of the coatings that we tested consisted of randomly distributed micropits. However, the correlation between our data and the term $T_m\sqrt{C_pKt}$ may be coincidental. Plotting of additional published data[4,5] against $T_m\sqrt{C_pKt}$ produces a graph of randomly distributed points, with rather complete mixing of data for oxides and fluorides.

## VI. Damage Thresholds of HR Coatings

In Fig. 3 are thresholds measured for HR coatings made of 13 combinations of the materials that were tested as single-layer films. Four reflectors of each type were tested, two made in each of two coating runs. Each reflector had a minimum of 15 quarterwave-thick layers and was overcoated with a halfwave-thick layer of the low-index material used in the reflector stack.

The thresholds fell into three groups: below 3 J/cm$^2$, between 3 and 5 J/cm$^2$, and greater than 5 J/cm$^2$. It is interesting that the largest thresholds observed for HR coatings were significantly less than the very large thresholds observed in single layers of the best low-index films, and greater than the thresholds for single layers of the relevant high-index materials.

Because each reflector contains two materials, and because we measured several parameters for films of each of the materials, there are many possible correlations between thresholds of HR coatings and material properties. We .elieve the principal correlations are described by the following statements: (1) There was a reasonable correlation between reflector thresholds and three properties of the high-index material used in the reflector: position of the UV edge, extinction coefficient and laser-damage threshold. Refractive index, stress, and environmental stability of high-index films did not correlate with reflector thresholds. (2) When various low-index materials were used with a particular high-index material, highest reflector thresholds were always obtained by minimizing refractive index for the low-index material. Among other properties measured on single layers of low-index materials, absorption, position of the UV edge, and stress were reasonably accurate indicators of the merits of the low-index materials for use in HR coatings, whereas threshold, cosmetic appearance and environmental stability of low-index single layers were sometimes inaccurate or inconclusive indicators of HR performance.

## VII. Thresholds of AR Coatings

Damage thresholds for AR coatings made from five combinations of materials are given in Fig. 4. For each combination, we tested four samples, two made in each of two coating runs. The coatings contained from three to six layers, and were deposited over a halfwave-thick undercoat layer of the low-index material used in the coating. The only exception was the $SiO_2/MgF_2$ coatings which were deposited over an $SiO_2$ undercoat.

Median thresholds for the five designs ranged from 4.5 to 6.1 $J/cm^2$. Since low-index materials generally have a higher damage threshold, it is interesting that coatings of a design having both high- and low-index materials, $Sc_2O_3/SiO_2$, had thresholds equal to those of AR coatings containing only low-index materials, $MgF_2$ and $SiO_2$. The only parameter measured on single-layer films which correlated with thresholds of AR coatings was stress. We suspect this correlation is accidental, because stress and thresholds were not correlated in either HR coatings or single-layer films.

## VIII. Summary

For single-layer coatings, thresholds were correlated with coating absorption, position of the UV absorption edge of the film material, and to some extent with refractive index, but were not correlated with stress, cosmetic appearance, or environmental stability. The HR coatings with the greatest thresholds were those made by pairing the high-index material with least absorption and highest threshold with the low-index material with lowest index. In AR coatings, thresholds were not correlated with any measured property of single-layer films other than stress, which is probably an accidental correlation since stress did not correlate with thresholds in either single-layer films or HR coatings.

The survey was reasonably successful, therefore, in identifying film parameters that are important in fabrication of damage-resistant UV films. The most critical factor is choice of a high-index material which is highly transparent in the UV; this is hardly surprising. However, it is of value to know that one is not constrained to use only those materials which can be deposited as cosmetically attractive coatings which have low stress and good environmental stability.

## IX. Acknowledgments

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Figure Captions

Fig. 1. Thresholds measured with 248-nm, 20-ns pulses on single-layer films of candidate UV materials. Optical thickness of each film was 124 nm.

Fig. 2. Dependence of thresholds of single-layer films on: a) extinction coefficient, b) position of the UV absorption edge, c) index of refraction, and d) film stress. Films with absorption edge at wavelengths << 200 nm and at wavelengths < 200 nm were arbitrarily plotted at, respectively, 194 and 196 nm. Compressive stress is taken to be positive in sign, and tensile stress to be negative.

Fig. 3 Thresholds measured with 248-nm, 20-nm pulses in HR coatings made from 13 combinations of high- and low-index materials.

Fig. 4. Thresholds measured with 248-nm, 20-ns in AR coatings made from 5 combinations of materials.

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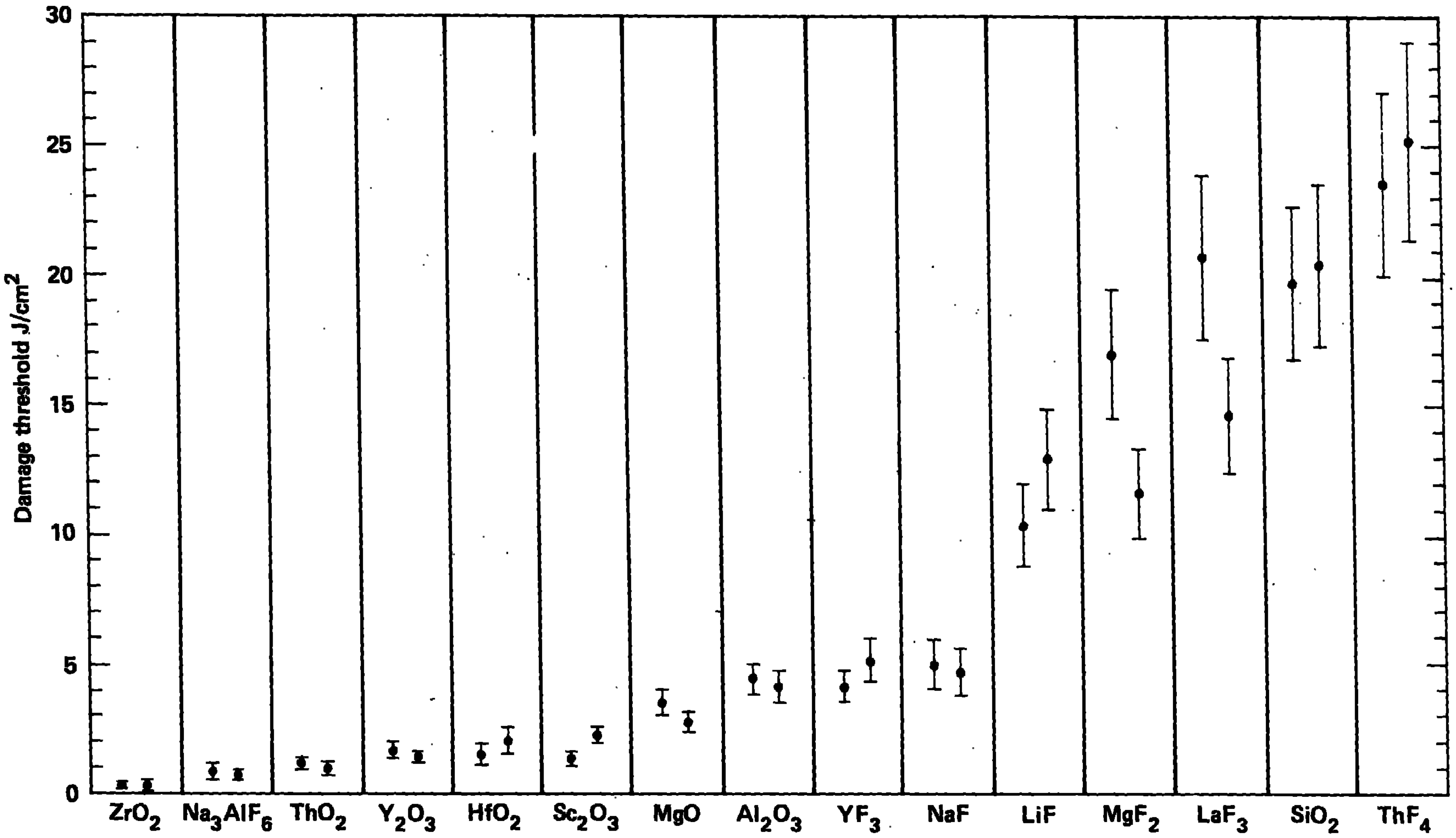
TABLE 1

Physical Properties of Single-Layer Films with Optical Thickness of 124 nm

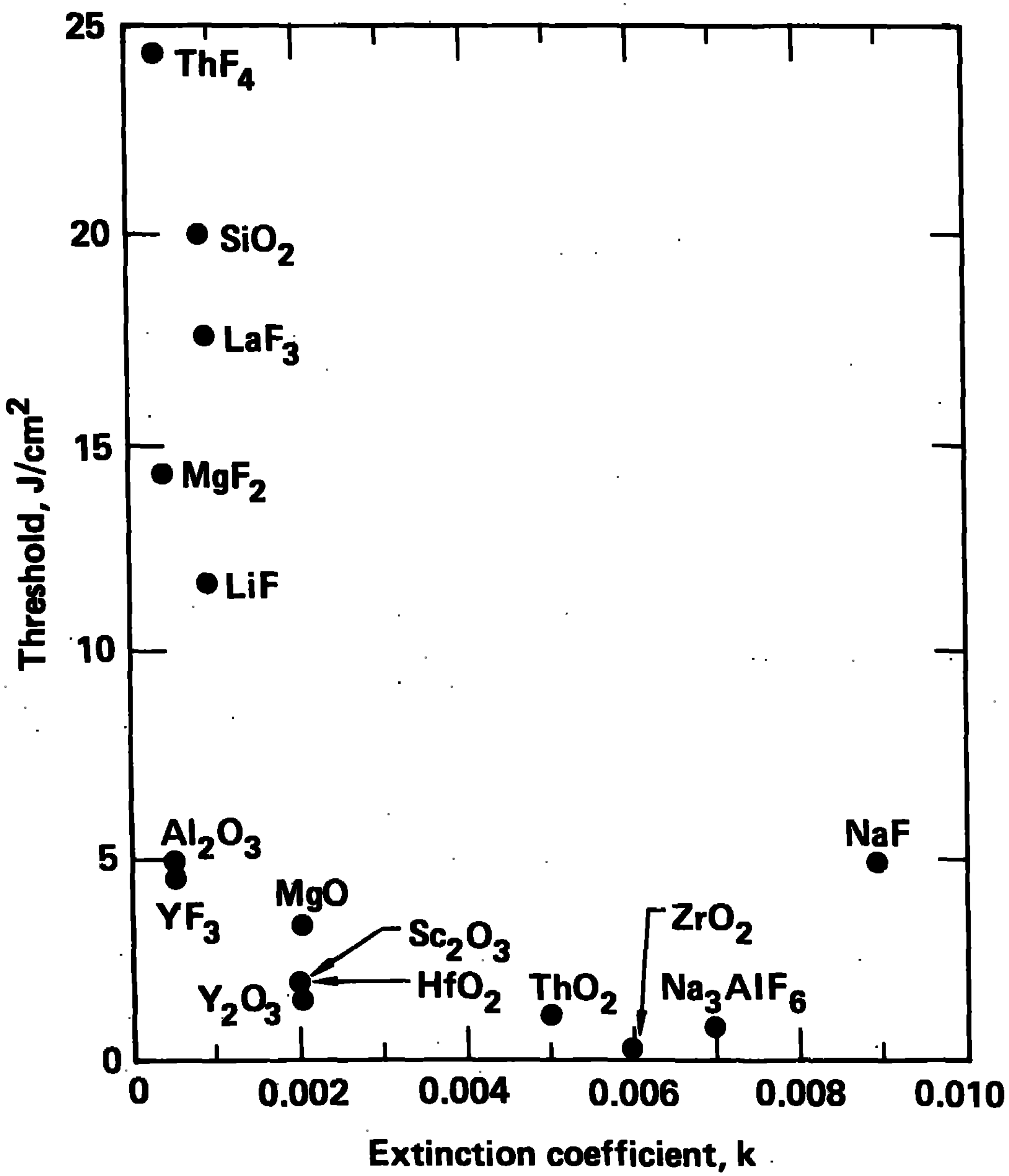
| Material[1] | Extinction Index (n) at 248 nm | Attenuation Coefficient (k) at 248 nm | Absorption Band[2] Edge, nm | Stress[3] KPSI | Environmental Stability |
|---|---|---|---|---|---|
| $ZrO_2$ | 2.25 | .006 | 230 | -39 | Pass |
| $Na_3AlF_6$ | 1.35 | .007 | S | -4 | Fail |
| $ThO_2$ | 1.90 | .005 | 200 | -72 | Pass |
| $Y_2O_3$ | 2.10 | .002 | 210 | +11 | Pass |
| $HfO_2$ | 2.25 | .002 | 215 | -59 | Pass |
| $Sc_2O_3$ | 2.11 | .002 | 205 | -23 | Pass |
| MgO | 1.83 | .002 | 200 | -5 | Fail |
| $Al_2O_3$ | 1.72 | < .001 | < 200 | -86 | Fail |
| $YF_3$ | 1.54 | < .001 | < 200 | -49 | Pass |
| NaF | 1.35 | .009 | S | -8 | Fail |
| LiF | 1.37 | .001 | << 200 | -1 | Marginal |
| $MgF_2$ | 1.43 | < .001 | < 200 | -50 | Pass |
| $LaF_3$ | 1.59 | .001 | < 200 | -91 | Pass |
| $SiO_2$ | 1.44 | .001 | < 200 | +4 | Pass |
| $ThF_4$ | 1.59 | < .001 | << 200 | -30 | Pass |

1. Materials are arranged in order of increasing threshold. (See Fig. 1.)
2. Absorption edge is 50% point in transmission; < 200 means some absorption at 200 nm; << 200 means no absorption at 200 nm; S means absorption edge probably masked by scattering.
3. +, compressive; -, tensile.



Damage threshold J/cm$^2$
30
25
20
15
10
5
0
$ZrO_2$
$Na_3AlF_6$
$ThO_2$
$Y_2O_3$
$HfO_2$
$Sc_2O_3$
MgO
$Al_2O_3$
$YF_3$
NaF
LiF
$MgF_2$
$LaF_3$
$SiO_2$
$ThF_4$


Figure 1



Threshold, J/cm2
25
20
15
10
5
0
ThF4
SiO2
LaF3
MgF2
LiF
Al2O3
YF3
MgO
Sc2O3
HfO2
Y2O3
ThO2
ZrO2
Na3AlF6
NaF
0
0.002
0.004
0.006
0.008
0.010
Extinction coefficient, k


Figure 2a

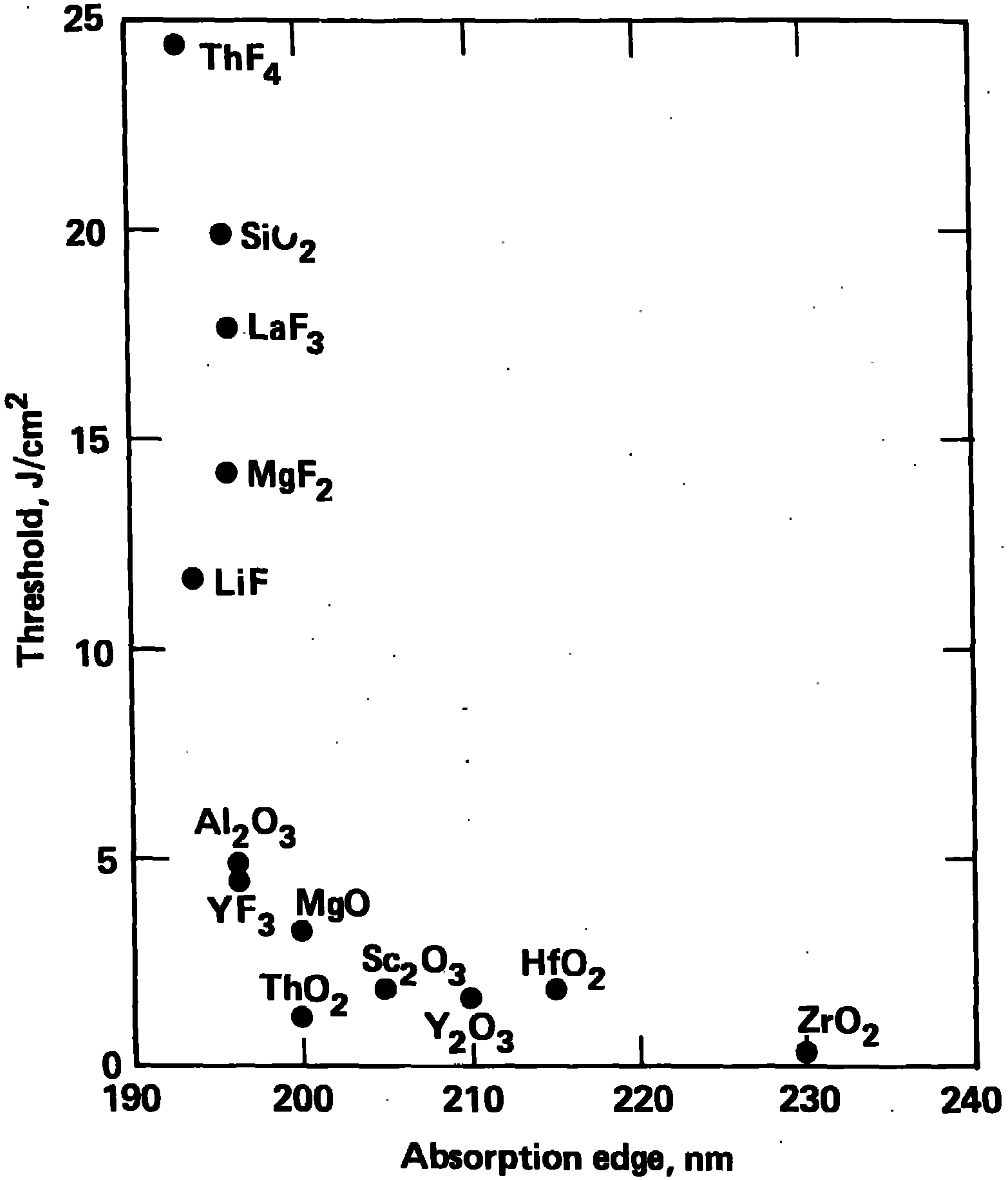
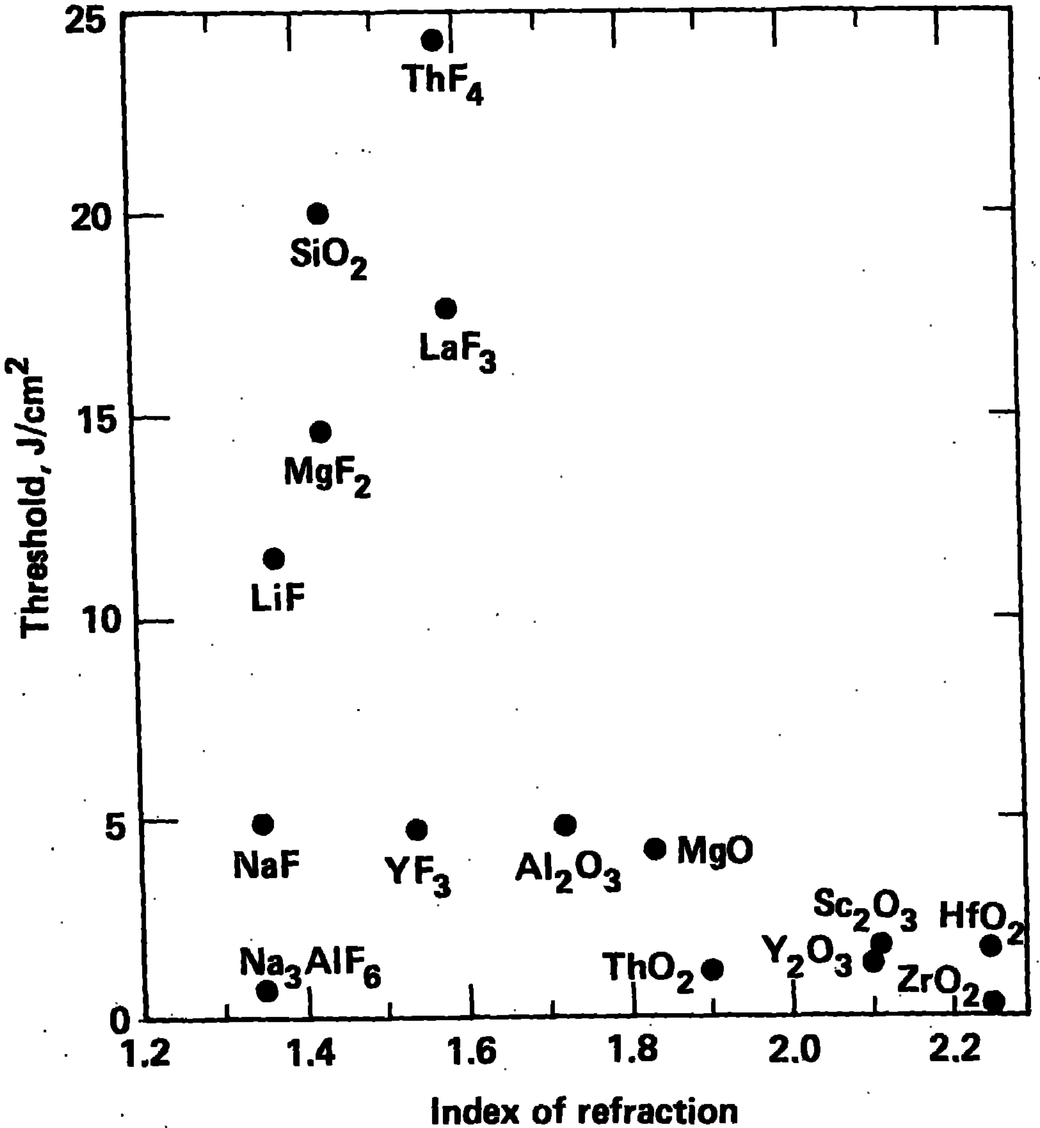
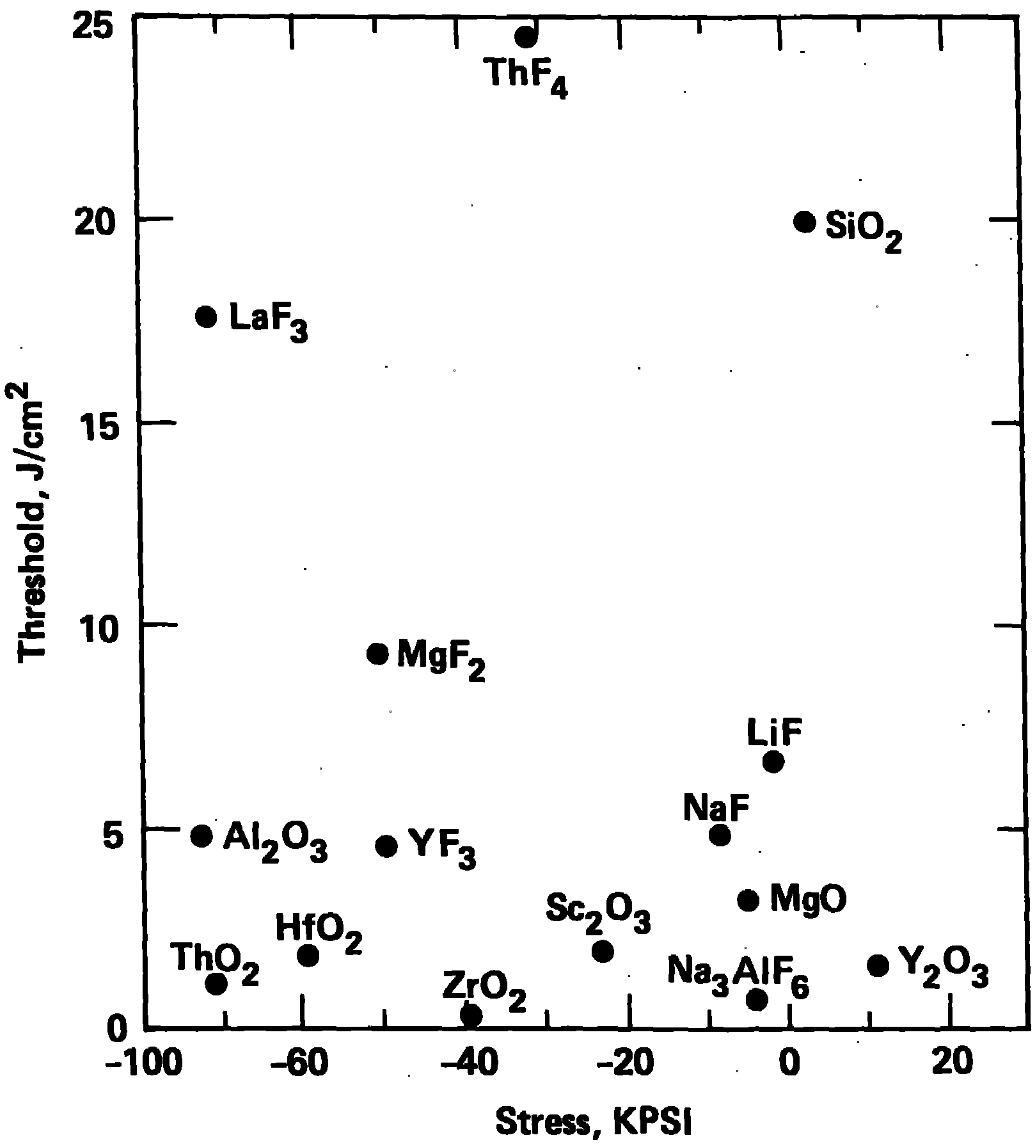

25
20
15
10
5
0
Threshold, J/cm$^2$
190
200
210
220
230
240
Absorption edge, nm
$ThF_4$
$SiO_2$
$LaF_3$
$MgF_2$
LiF
$Al_2O_3$
$YF_3$
MgO
$ThO_2$
$Sc_2O_3$
$Y_2O_3$
$HfO_2$
$ZrO_2$

Figure 2b



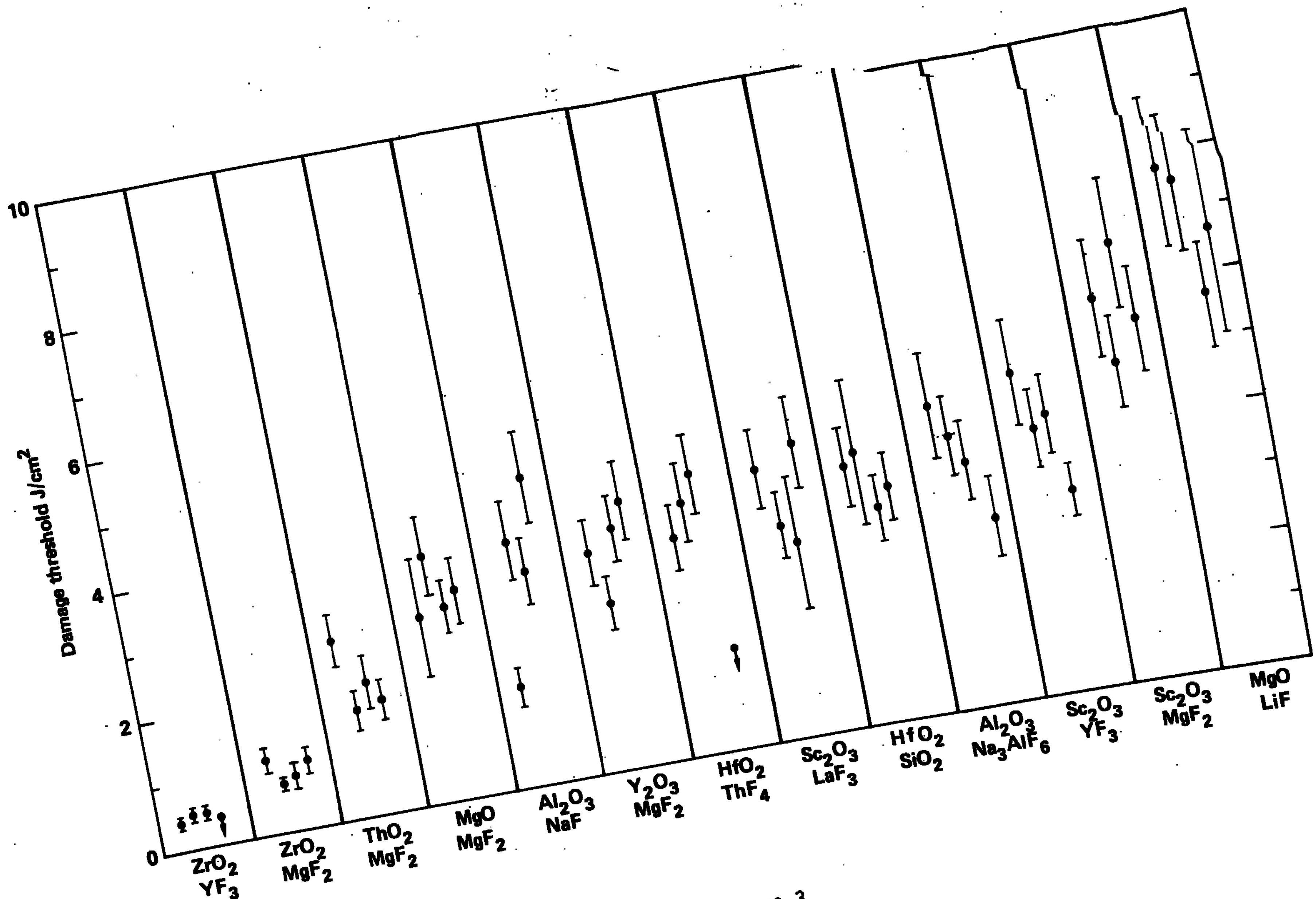
ThF4
SiO2
LaF3
MgF2
LiF
NaF
YF3
Al2O3
MgO
Sc2O3
HfO2
Na3AlF6
ThO2
Y2O3
ZrO2
25
20
15
10
5
0
1.2
1.4
1.6
1.8
2.0
2.2
Threshold, J/cm2
Index of refraction


Figure 2c



ThF4
SiO2
LaF3
MgF2
LiF
NaF
Al2O3
YF3
MgO
Sc2O3
HfO2
ThO2
ZrO2
Na3AlF6
Y2O3
25
20
15
10
5
0
-100
-60
-40
-20
0
20
Threshold, J/cm2
Stress, KPSI


Figure 2d



Damage threshold J/cm²
0
2
4
6
8
10
ZrO2 YF3
ZrO2 MgF2
ThO2 MgF2
MgO MgF2
Al2O3 NaF
Y2O3 MgF2
HfO2 ThF4
Sc2O3 LaF3
HfO2 SiO2
Al2O3 Na3AlF6
Sc2O3 YF3
Sc2O3 MgF2
MgO LiF


Figure 3

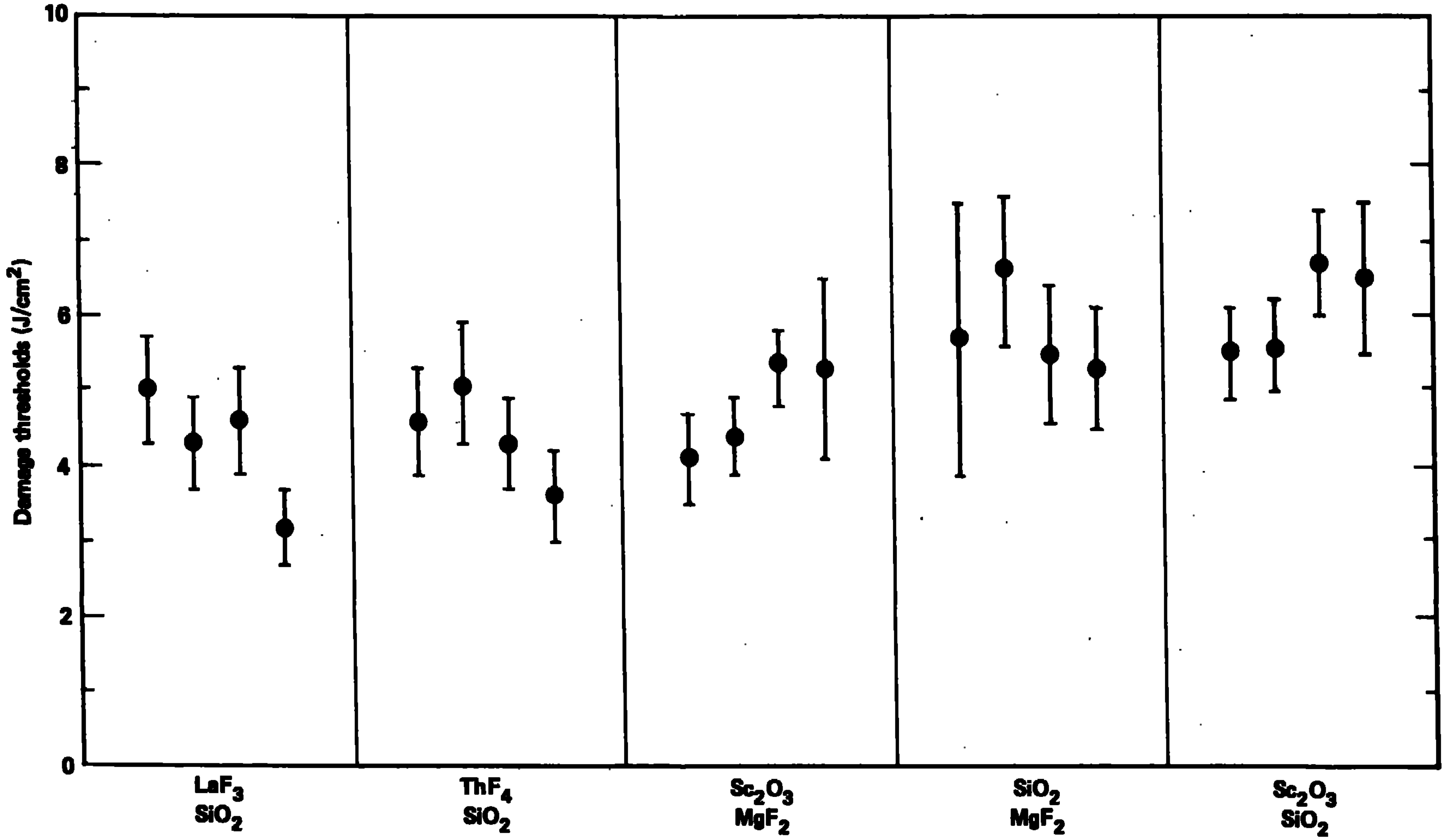

10
8
6
4
2
0
Damage thresholds (J/cm²)
LaF₃ SiO₂
ThF₄ SiO₂
Sc₂O₃ MgF₂
SiO₂ MgF₂
Sc₂O₃ SiO₂

Figure 4